# Modeling and Optimization of Phosphate Recovery from Industrial Wastewater and Precipitation of Solid Fertilizer using Experimental Design Methodology

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In this work, the experimental design methodology is applied to optimize phosphate salts precipitation as struvite and others applied in soil fertilization from treated industrial wastewater stream. This is a process to maximize phosphate recovery percentage from inlet wastewater stream containing interfering foreign ions. Therefore, these optimized conditions could be used as input data for engineering design-software for successive equipment required in wastewater treatment plant. A four factors Box–Behnken experimental design was used to model and optimize the operating parameters. The optimum operating conditions were quite efficient in trapping 86.10 % recovered phosphates in industrial stream, and 92.6 % in synthetic solution at pH of 10.89, time of reaction of 34.76 min, temperature of 25.23 °C and R of 2.25 with an insignificance effect for molar ratio (*R*) between Mg and PO<sub>4</sub> ions. If these optimal parameters were shifted, the reached recovery percentage would decrease with the precipitated struvite.

The precipitated salts were subjected to characterization through different chemical techniques confirming the presence of struvite with schertelite as a mixed slow release fertilizer.

Key words:

wastewater treatment, calcium interference, surface response, design methodology, phosphorous depletion

# Introduction

Phosphorus (P) is one of the primary nutrients generating eutrophication in aquatic systems<sup>1</sup>. To prevent eutrophication, municipal or agricultural wastewaters are treated to reduce the phosphorus concentrations in the wastewater reaching surface water streams. While unregulated P is a pollutant in a water body, phosphorous is a useful resource in agricultural fertilizers, food supply, and industrial raw materials<sup>1-3</sup>. Unfortunately, phosphorous resources have mostly been obtained from minerals that will definitely be limited by the recent enormous utilization. Based on a previous study<sup>4</sup>, phosphorous mineral resources are economically feasible for only 50 years. Therefore, P recovery from wastewater can be advantageous with respect to preventing water pollution, removing scales on the inner surface of pumps and pipes, facilitating successive treatment steps, and preventing the devastation of mineral resources<sup>4,5</sup>.

Successful P recovery should require an effective nucleation and growth of struvite crystals so that desirable amounts of precipitated struvite can be recovered typically through the gravitational settling process. However, there are challenges to overcome; for example, calcium ions (Ca<sup>2+</sup>), of which the typical concentrations are 30–60 mg L<sup>-1</sup> in municipal wastewater plants, are known as representative ions that hamper struvite crystal nucleation and growth<sup>6</sup>. Calcium ions actively react with phosphate to form calcium phosphates. Previous studies on the influence of calcium on struvite crystallization reported that Calcium ions with struvite co-precipitation can retard the nucleation induction and inhibit the growth for struvite crystal formation<sup>6,7</sup>.

However, calcium, as an impurity, could be a negative factor for struvite formation. Calcium presence at high levels in synthesized wastewater would inhibit struvite formation, because calcium-phosphorus precipitates could also be formed.

In theory, struvite precipitation could occur in wastewater effluent if phosphorus were released into solution, as reactive phosphate ions, and become available for struvite formation. In this study,

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the liberation of phosphorus from calcium-phosphate solids was investigated using different methods, such as acidification and sequestering calcium with a chelating agent. The effect of various conditions, such as pH change, on the liberation of phosphorus and calcium was also investigated. An improved process for phosphorus recovery from anaerobically digested dairy effluent through struvite crystallization was proposed. Phosphorus, as suspended calcium phosphate solids in anaerobic digestion dairy manure effluent, was liberated into a solution as phosphate ions by either acidification or adding an EDTA chelating agent. Approximately 91 % of the total phosphorus and 93 % of the calcium were released into the solution by the addition of EDTA<sup>8,9</sup>.

The calcium impurity was precipitated to a minimum using ammonium oxalate and oxalic acid<sup>9,10</sup>. Many factors could affect the efficiency of chemical precipitation, including pH, temperature, time starting molar ratio, and stirring rate. Therefore, multiple variables may influence the extraction efficiency, and the response surface methodology (RSM) is an effective technique for optimizing the process<sup>11</sup>.

The methodology of the experimental design software makes it possible to adapt the experimentation needed to optimize many parameters in the most efficient way<sup>12</sup>.

Once the experimental domain D is established with a number of factors (k factors), represented by the codified variables  $(x_1, x_2, ..., x_k)$  and a polynomial model is proposed, then designs for practical experiments exist, i.e. sets of experimental conditions, which provide the estimates of less variance for coefficients and response. A polynomial model, with p + 1 coefficient, is proposed to relate the experimental response to be optimized, y, with the k factors through the **p** variables ( $p \ge k$ ) as shown in Eq.1.

$$Y_{i} = b_{0} + b_{1}x_{1} + b_{2}x_{2} + \dots + b_{k}x_{k} + + b_{11}x_{1}^{2} + b_{22}x_{2}^{2} + \dots + b_{kk}x_{k}^{2} + (1) b_{12}x_{1}x_{2} + \dots + b_{1k}x_{1}x_{k} + \dots + b_{k-1,k}x_{k-1}x_{k}x_{1}$$

where

 $x_{\rm k+1},\!x_{\rm k+2},\,\ldots,\,x_{\rm p}$  are the cross-products and powers of the k factors,

Table 1 – Initial composition of industrial wastewater stream

 $x_1, x_2, \dots, x_k$ , are the codified factors.

Central composite, Dohelert and Box Behnken designs are widely used and allow the researcher to choose the most suitable one for approaching the optimization problem<sup>13–17</sup>.

Struvite (MgNH<sub>4</sub>PO<sub>4</sub> · 6H<sub>2</sub>O) precipitation from industrial wastewater streams occurs under certain environmental conditions of pH, alkalinity, temperature, phosphorus, ammonium and magnesium concentrations which vary with water source and interfering ions presence. The objective of this work was to model and optimize the operating parameters for maximum phosphate recovery by chemical precipitation of struvite from industrial wastewater effluents (pH, Mg: PO<sub>4</sub> starting molar ratio *R*, temperature, and time of reaction) using experimental design methodology.

We also compared the effect of foreign ions on produced phosphate salts by using a synthetic solution simulating the same concentration of magnesium, ammonium and phosphate ions in waste water streams.

# Materials and methods

### **Materials**

Large volume samples were taken from the mixed effluent stream of a nitric acid factory in Suez (a chemical and fertilizer company), and then treated chemically to decrease calcium content to a minimum, as shown in Table 1.

Double-distilled deionized water was used in all experiments. Analytical grade ammonium sulfate, potassium di-hydrogen phosphates, and sodium hydroxides were supplied from El-Gomhoria Company for chemicals and pharmaceuticals. Liquid Bittern (LB) as a low cost source of magnesium was kindly supplied from table salt manufacturers and treated by chemical methods to remove calcium, with the composition as shown in Table 2.

### **Experimental analysis**

The composition of mixed effluent from nitric acid factory in Suez Company for chemicals and fertilizers, listed in Table 1, was analyzed according to standard methods for examination of water and wastewater (for ammonia, nitrite, magnesium, hardness, calcium, conductivity, pH value, dissolved solids and others).  $PO_4$  ions concentration in liquid filtrates for both industrial and synthetic wastewater

| pH value | PO <sub>4</sub> mg L <sup>-1</sup> | Ca mg L <sup>-1</sup> | NH <sub>4</sub> mg L <sup>-1</sup> | NO <sub>2</sub> mg L <sup>-1</sup> | Mg mg L <sup>-1</sup> | TDS  | Conductivity<br>(mS cm <sup>-1</sup> ) |
|----------|------------------------------------|-----------------------|------------------------------------|------------------------------------|-----------------------|------|--|
| 3.44     | 260                                | 2.14                  | 0.085                              | 0.656                              | 5.57                  | 2960 | 4.2                                    |

| magnesium                   |              |
|-----------------------------|--------------|
| Value (mg L <sup>-1</sup> ) | Element      |
| 292                         | TDS          |
| 1.6                         | Calcium      |
| 73.84                       | Magnesium    |
| 21.76                       | Sodium       |
| 218.63                      | Chlorides    |
| 3.3                         | Sulfates     |
| 0.5                         | Carbonates   |
| 9.81                        | Potassium    |
| 1.73                        | Bicarbonates |
| 12                          | Bromine      |
| 70                          | Boron        |
| 5                           | Iodine       |
| 0.31                        | Lithium      |
| 456 μS cm <sup>-1</sup>     | Conductivity |
|                             |              |

Table 2 – Characteristics of liquid bitten used as a source of magnesium

streams were analyzed using the double-beam UV spectrophotometer Agilent cary100. Precipitated phosphate salts were subjected to PAN analytical X-ray Diffraction equipment model X'pert PRO with monochromator, Cu radiation ( $\lambda = 1.542$  Å) at 50 KV, 40 mA, and scanning speed of 0.02° sec.  $^{-1}$ were used. The reflection peaks between  $2\theta = 2^{\circ}$ and  $60^{\circ}$ , corresponding spacing (d, Å) and relative intestines  $(I/I^{\circ})$  were obtained and compared with ICDD libraries. Energy-dispersive X-ray fluorescence (EDIX) device made in Oxford contained DET, area-10 mm<sup>2</sup>, window (ATW2) model 6587, was also used to analyze precipitated salts elementally for different ions. Phosphate salts samples were grounded and coated with gold sputtering to provide electrical conductivity. The micrographs were taken on a JEOL 5410 scanning electron microscope at 20 kV.

### **Experimental technique**

A 15 L volume of industrial wastewater sample was treated with 30 mmol oxalic acid/ammonium oxalate to chelate and capture calcium from the solution and thus free the total phosphorous present (260 mg L<sup>-1</sup>)<sup>8</sup>, and the de-calcinated water was re-analyzed to obtain the initial concentration for different ions (Table 1) required for struvite precipitation and phosphate removal. A solution containing only PO<sub>4</sub><sup>3-</sup> [260 mg L<sup>-1</sup>], Mg<sup>2+</sup> [5.57 mg L<sup>-1</sup>] and NH<sub>4</sub><sup>+</sup> [0.065 mg L<sup>-1</sup>] was synthetized from analytical grade potassium di-hydrogen phosphates, magnesium chloride, and ammonium chloride, to investigate the effect of foreign ions of nitrite, and

remaining calcium on struvite precipitation and phosphates percentage recovery.

The experimental protocol was as follows:

1. A predetermined mass of ammonium chloride and volume of de-calcinated bittern were added to each industrial and synthetic wastewater volume of 600 mL to adjust the concentration of Mg:PO<sub>4</sub>:NH<sub>4</sub> to the studied molar ratio.

2. Adjust wastewater pH (10-11) using 200 mg  $L^{-1}$  solution of sodium hydroxide.

3. Allow the solution (600 mL) to precipitate struvite in a time of reaction from 20 to 60 minutes at a low stirring rate (60 rpm) using a WiseStir – jar tester with digital control stabilized in all sets of reactions for suitable struvite precipitation and crystal growth, as shown in Figure 1.

4. Allow solid product to crystallize for 2-hours without agitation.

5. Filter the mixture using a vacuum filtration system to retrieve the liquid phase using a glass-vacuum set-up with a Rocker 400 vacuum pump (Figure 1).

6. Analyze the filtrate for remaining  $PO_4$  ions using double beam spectrophotometer Agilent cary100, and perform XRD, and SEM analysis of the naturally-dried solid salts for optimum conditions sample.

The same aforementioned procedure was repeated on a wastewater synthetic solution with different  $Mg:PO_4:NH_4$  molar ratios for maximum phosphorous recovery with the precipitation of fertilizer crystals. The optimum precipitation time, media pH, initial molar ratio, and precipitation temperature were used as input data in the design of an industrial multi-purpose reactor for struvite precipitation and filtration, which is proposed to be implemented in the factory-extension area.

### **Results and discussion**

### Properties of solid precipitated crystals

The filtrate liquid solution was subjected to double beam UV-spectrophotometer for remaining phosphorous ions analysis. The corresponding solid crystals were subjected to X-Ray Diffraction (XRD) as shown in Figures 2 and 3, SEM in Figure 4, and EDIX in Figure 5, to show its characterization and chemical composition.

By comparing Figures 2 and 3, obvious is the presence of schertilite (MgNH<sub>4</sub>PO<sub>4</sub>  $\cdot$  4H<sub>2</sub>O) with a small percentage of struvite (MgNH<sub>4</sub>PO<sub>4</sub>  $\cdot$  6H<sub>2</sub>O) and other phosphate salts in the industrial wastewater streams.on the other hand, Figure 3 gives more clearly pure struvite crystals for synthetic solution, showing the effect of foreign ions interference on on phosphate precipitates.

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# Precipitation system

Vacuum filtration system

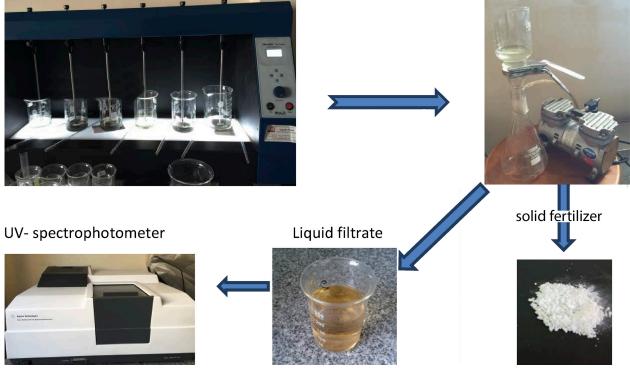


Fig. 1 – Experimental and analytical set-up for struvite precipitation and phosphate recovery

It is clear from Figure 4 that the precipitated salts were agglomerated, indicating the presence of schertilite and struvite superimposed over each other with small-sized crystals, which was differentiated from pure struvite precipitated as needle shape. This was confirmed again by EDIX analysis in Figure 5, showing the percentage of each element in solid precipitates.

Economic return of this process was previously studied<sup>19</sup>, we can conclude that the yield of mixed phosphate fertilizers with struvite will be profitable if it will be sold and so this will decrease phosphate -fertilizers demands.

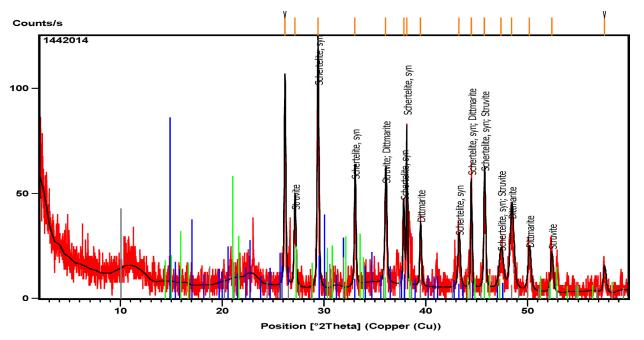


Fig. 2 – XRD pattern for precipitated phosphate salts (solid fertilizers) from industrial wastewater streams

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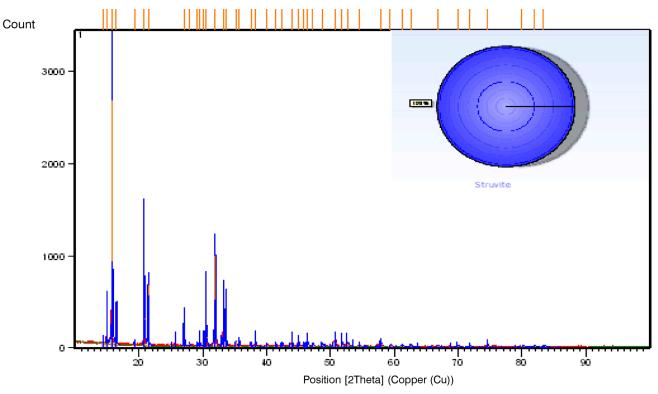


Fig. 3 – XRD pattern for precipitated phosphate salts as struvite from synthetic solution

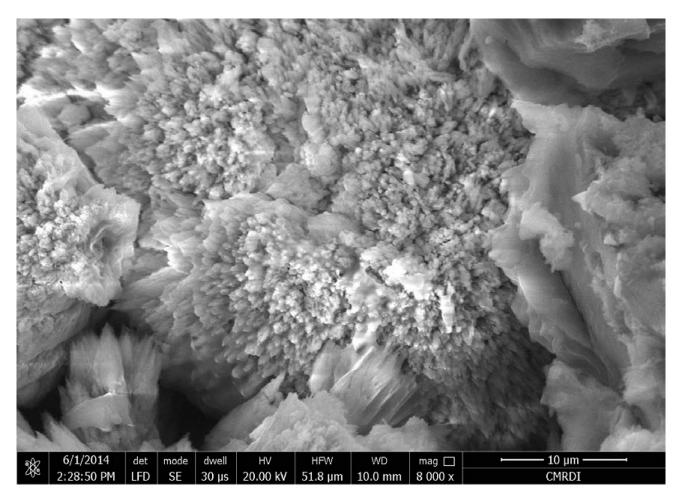


Fig. 4 – SEM for precipitated phosphate salts as struvite and schertilite from industrial stream

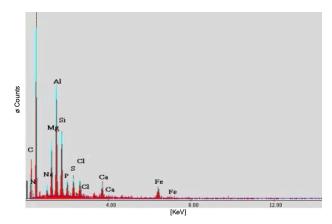


Fig. 5 – *EDIX* analysis graph with its data for precipitated phosphate salts as struvite and schertilite from industrial stream

### Studied factors and experimental domains

Four factors and their fields were adopted in this study (illustrated in Table 3). The chosen responses were PO<sub>4</sub> conc. expressed as percentage recovery from inlet concentration for both industrial and synthetic wastewater streams, designated by  $Y_1$  (Ind.) and  $Y_2$  (Syn.).

Table 3 – Studied factors and experimental domains

| Effect                | Factors                             | -1  | 0    | +1 | Increment |
|-----------------------|-------------------------------------|-----|------|----|-----------|
| <i>X</i> <sub>1</sub> | Temperature ( $T$ ) °C              | 15  | 26.5 | 38 | 11.5      |
| $X_2$                 | Time of reaction ( <i>t</i> ), min. | 20  | 40   | 60 | 20        |
| $X_3$                 | рН                                  | 10  | 10.5 | 11 | 0.5       |
| $X_4$                 | Molar ratio $(R) = (Mg:PO_4)$       | 1.5 | 2.25 | 3  | 0.75      |

These four parameters were selected according to previous literature<sup>6,9,18</sup> as the most controlling parameters for phosphate recovery and struvite precipitation but their ranges were tested preliminarily through this work for this special case of industrial wastewater streams.

### **Experimental matrix and models**

The purpose of this work was to model and optimize the selected responses  $Y_1$  and  $Y_2$ . A Box-Behnken matrix seemed necessary to achieve this goal (Table 3). As indicated in this table, the Box-Behnken design is built on sixteen (four factors: 2n+1 = 25 = 32) from 1 to 24 experiences (levels +1, 0 and -1) and eight identical repeated tests performed at the center and named center points (level zero) (from 25 to 32) with the purpose of calculating the experimental variance. The recovered percentage of phosphates from both industrial and synthetic wastewater streams obtained from all the experiments are listed in Table 4.

The experimental data obtained were analyzed by the response surface regression procedure using the following second-order polynomial equation:

$$Y_{i} = b_{0} + \sum_{i=1}^{\infty} (b_{i}X_{i}) + \sum_{\substack{i=1\\k=1}}^{\infty} (b_{ik}X_{i}X_{k}) + \sum_{i=1}^{\infty} (b_{ii})(X_{i})^{2}$$

where  $Y_i$  is the chosen response i,  $b_0$  is a constant, and  $b_i$ ,  $b_{ii}$ ,  $b_{ik}$  are the linear, quadratic and interactive coefficients, and the estimation of the significant factor i and  $X_i$  is its level. Three-dimensional surface response plots were generated using the fitted model by varying two variables within the experimental range and holding the others constant at the central point. The coefficients of the response surface equation were estimated by using the NemrodW software. The test of statistical significance was based on the total error criteria with a confidence level of 95.0 %.

Table 5 summarizes the factor effects estimation for the two responses.

As evident, the significant factors are: temperature  $(b_1)$ , reaction time  $(b_2)$ , pH  $(b_3)$ , three quadratic terms  $(b_{11}, b_{22}, b_{33})$ , and two interaction terms  $(b_{13}$ and  $b_{23})$  to the response % PO<sub>4</sub> Ind  $(Y_1)$ . Temperature  $(b_1)$ , reaction time  $(b_2)$ , pH  $(b_3)$ , two quadratic terms  $(b_{11}, b_{22})$ , and two interaction terms  $(b_{12}$  and  $b_{13})$  to the response % PO<sub>4</sub> Syn  $(Y_2)$ .

The resulting models are given by the following equations:

$$Y_{1} = b_{0} + (b_{1}X_{1} + b_{2}X_{2} + b_{3}X_{3}) + + (b_{13}X_{1}X_{3} + b_{23}X_{2}X_{3}) + + (b_{11}(X_{1})^{2}) + (b_{22}(X_{2})^{2}) + (b_{33}(X_{3})^{2})$$

$$Y_{1}(\%PO_{4}Ind) =$$

$$= 78.75 + (-8.394X_{1} - 3.02X_{2} + 14.21X_{3}) +$$

$$+ (7.185X_{1}X_{3} - 6.148X_{2}X_{3}) + (-15.586(X_{1})^{2}) +$$

$$+ (-3.886(X_{2})^{2}) + (-4.748(X_{3})^{2})$$

$$Y_2 = b_0 + (b_1X_1 + b_2X_2 + b_3X_3) + (b_{12}X_1X_2 + b_{13}X_1X_3) + (b_{11}(X_1)^2) + (b_{22}(X_2)^2)$$

$$Y_{2}(\% PO_{4}Syn) =$$

$$= 80.909 + (-16.271X_{1} - 5.784X_{2} - 3.723X_{3}) +$$

$$+ (+15.615X_{1}X_{2} - 12.22X_{1}X_{3}) +$$

$$+ (-28.151(X_{1})^{2}) + (-12.139(X_{2})^{2})$$

| Table 4 - Box | -Behnken matri | x and results |                     |          |  |  |
|---------------|----------------|---------------|---------------------|----------|--|--|
| No. of exp.   | $T(X_1)$       | $t(X_2)$      | pH(X <sub>3</sub> ) | $R(X_4)$ | % Recovery<br>[PO <sub>4</sub> ] (Ind) ( $Y_1$ ) exp | % Recovery<br>$[PO_4]$ (Syn) ( $Y_2$ ) exp |
| 1             | -1             | -1            | 0                   | 0        | 71.60  | 74.43                                      |
| 2             | 1              | -1            | 0                   | 0        | 40.82  | 26.52                                      |
| 3             | -1             | 1             | 0                   | 0        | 77.15  | 32.073                                     |
| 4             | 1              | 1             | 0                   | 0        | 36.51  | 46.65                                      |
| 5             | -1             | 0             | -1                  | 0        | 50.00  | 68.20                                      |
| 6             | 1              | 0             | -1                  | 0        | 25.06  | 72.85                                      |
| 7             | -1             | 0             | 1                   | 0        | 85.36  | 62.71                                      |
| 8             | 1              | 0             | 1                   | 0        | 89.16  | 18.48                                      |
| 9             | -1             | 0             | 0                   | -1       | 84.50  | 81.14                                      |
| 10            | 1              | 0             | 0                   | -1       | 83.44  | 13.13                                      |
| 11            | -1             | 0             | 0                   | 1        | 39.65  | 67.14                                      |
| 12            | 1              | 0             | 0                   | 1        | 32.54  | 12.84                                      |
| 13            | 0              | -1            | -1                  | 0        | 56.97  | 65.61                                      |
| 14            | 0              | 1             | -1                  | 0        | 57.71  | 53.36                                      |
| 15            | 0              | -1            | 1                   | 0        | 92.41  | 83.71                                      |
| 16            | 0              | 1             | 1                   | 0        | 68.56  | 69.54                                      |
| 17            | 0              | -1            | 0                   | -1       | 73.37  | 67.85                                      |
| 18            | 0              | 1             | 0                   | -1       | 55.63  | 52.91                                      |
| 19            | 0              | -1            | 0                   | 1        | 87.54  | 68.73                                      |
| 20            | 0              | 1             | 0                   | 1        | 91.12  | 62.88                                      |
| 21            | 0              | 0             | -1                  | -1       | 53.83  | 89.53                                      |
| 22            | 0              | 0             | 1                   | -1       | 77.80  | 83.34                                      |
| 23            | 0              | 0             | -1                  | 1        | 72.40  | 86.28                                      |
| 24            | 0              | 0             | 1                   | 1        | 73.24  | 73.37                                      |
| 25            | 0              | 0             | 0                   | 0        | 81.65  | 82.00                                      |
| 26            | 0              | 0             | 0                   | 0        | 75.15  | 76.73                                      |
| 27            | 0              | 0             | 0                   | 0        | 77.39  | 77.63                                      |
| 28            | 0              | 0             | 0                   | 0        | 71.42  | 86.01                                      |
| 29            | 0              | 0             | 0                   | 0        | 78.05  | 83.24                                      |
| 30            | 0              | 0             | 0                   | 0        | 79.98  | 81.07                                      |
| 31            | 0              | 0             | 0                   | 0        | 80.91  | 75.98                                      |
| 22            | 0              | 0             | 0                   | 0        | 05.50  | 04 (1                                      |

85.50

84.61

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|---|----------------------------|
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|                        | Ind) and | $Y_2 (\% PO_4 Syn)$ |        | . ,           |
|------------------------|----------|---------------------|--------|---------------|
| Coefficient            | Value    | Standard deviation  | t-exp  | Signification |
| $Y_1$                  |          |                     |        |               |
| $b_{_0}$               | 78.756   | 1.519               | 51.85  | 0.01***       |
| Linear                 |          |                     |        |               |
| $b_1$                  | -8.394   | 1.240               | -6.77  | 0.0260***     |
| $b_2$                  | -3.002   | 1.240               | -2.42  | 4.60*         |
| $b_{3}$                | 14.213   | 1.240               | 11.46  | 0.01***       |
| $b_4$                  | -2.673   | 1.240               | -2.16  | 6.8           |
| Quadratic              |          |                     |        |               |
| $b_{11}^{}$            | -15.586  | 1.581               | -9.86  | 0.01***       |
| $b_{22}^{}$            | -3.886   | 1.581               | -2.46  | 4.36*         |
| <i>b</i> <sub>33</sub> | -4.748   | 1.581               | -3.00  | 1.98*         |
| $b_{_{44}}$            | -1.928   | 1.581               | -1.22  | 26.2          |
| Interaction            |          |                     |        |               |
| <i>b</i> <sub>12</sub> | -2.465   | 2.148               | -1.15  | 28.9          |
| <i>b</i> <sub>13</sub> | 7.185    | 2.148               | 3.35   | 1.23*         |
| b <sub>23</sub>        | -6.148   | 2.148               | -2.86  | 2.43*         |
| $b_{14}^{23}$          | -1.512   | 2.148               | -0.70  | 50.4          |
| <i>b</i> <sub>24</sub> | 5.330    | 2.148               | 2.48   | 4.21*         |
| b <sub>34</sub>        | -5.783   | 2.148               | -2.69  | 3.10*         |
| $R^2$                  | 0.596    |                     |        |               |
| Adj R <sup>2</sup>     | 0.578    |                     |        |               |
| <u>Y</u> 2             |          |                     |        |               |
| $b_0$                  | 80.909   | 1.392               | 60.89  | 0.01***       |
| $b_1$                  | -16.271  | 1.085               | -15.00 | 0.01***       |
| $b_2$                  | -5.784   | 1.085               | -5.33  | 0.109**       |
| $b_3$                  | -3.723   | 1.085               | -3.43  | 1.10*         |
| $b_4$                  | -1.388   | 1.085               | -1.28  | 24.1          |
| <i>b</i> <sub>11</sub> | -28.151  | 1.383               | -20.35 | 0.01***       |
| <i>b</i> <sub>22</sub> | -12.139  |                     | -8.78  |               |
| b <sub>33</sub>        | 3.97     | 1.383               | 2.31   |               |
| <i>b</i> <sub>44</sub> | -5.283   |                     | -3.82  |               |
| b <sub>12</sub>        | 15.615   | 1.879               | 8.31   |               |
| $b_{13}$               | -12.220  |                     | -6.50  |               |
| $b_{23}$               | -0.48    | 1.879               | -0.26  |               |
| $b_{14}^{23}$          | 3.428    |                     | 1.82   |               |
| b <sub>24</sub>        | 2.272    |                     | 1.21   |               |
| b <sub>34</sub>        | -1.680   | 1.879               | -0.89  |               |
| $R^2$                  | 0.814    |                     |        |               |
| Adjusted R             |          |                     |        |               |
| -                      |          |                     |        |               |

Table 5 – Factors signification for the two responses  $Y_1$  (%  $PO_4$ Ind) and  $Y_2$  (%  $PO_4$  Syn) Table 5 summarizes the signification of coefficients obtained giving higher signification level for  $b_1$ ,  $b_2$  and  $b_3$  which were the most affecting parameters<sup>19-21</sup>, indicating adequate accuracy and general availability of the polynomial model. The application of RSM (Response Surface Methodology) yielded the following regression equation which was an empirical relationship between % PO<sub>4</sub> Ind  $(Y_1)$  recovered from industrial wastewater streams and % PO<sub>4</sub> Syn  $(Y_2)$  recovered from synthetic solution and the test variables in coded units.

### Analysis of residue and variance

Figures 6 and 7 reveal the distribution of the calculated versus the experimental values for both responses ( $Y_1$  and  $Y_2$ ). Both figures show that the points are almost randomly distributed about the line representing exact agreement providing little evidence of lack-of-fit for both quadratic models. Thus, the model is valid. To confirm this validity, the analysis of variance was used (Table 6).

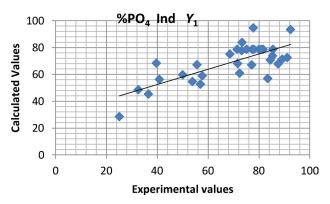


Fig. 6 – Calculated versus experimental values graph for % PO, for industrial wastewater stream

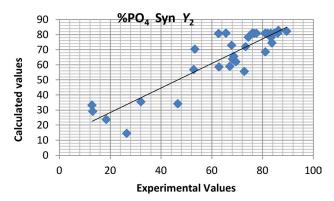


Fig. 7 – Calculated versus experimental values graph for  $% PO_4$  for synthetic solution

As evident, the main results for  $Y_1$  and  $Y_2$  are, respectively 444.32 and 272.47 as lack of fit mean square, and 18.45 and 11.10 as estimation of experimental variance. Thus, the values of the ratios be-

, \*\*, \*\*\* represent signification level

| Source of variation           | SS       | DF | MS     | Ratio | Signification |
|-------------------------------|----------|----|--------|-------|---------------|
| $Y_1$ , % PO <sub>4</sub> Ind |          |    |        |       |               |
| Regression                    | 6034.74  | 14 | 431.05 | 23.35 | 0.0163***     |
| Residual                      | 4572.44  | 17 | 268.96 |       |               |
| Lack of fit                   | 4443.26  | 10 | 444.32 | 24.0  | 0.0174***     |
| Pure error                    | 129.17   | 7  | 18.45  |       |               |
| Total                         | 10607.1  | 31 |        |       |               |
| $Y_2$ , % PO <sub>4</sub> Syn |          |    |        |       |               |
| Regression                    | 12534.50 | 14 | 895.32 | 80.62 | < 0.01***     |
| Residual                      | 2802.48  | 17 | 164.85 |       |               |
| Lack of fit                   | 2724.74  | 10 | 272.47 | 24.53 | 0.0164***     |
| Pure error                    | 77.73    | 7  | 11.10  |       |               |
| Total                         | 15337    | 31 |        |       |               |

Table 6 – Variance analysis

\*, \*\*, \*\*\* represent signification level

SS - Sum of Squares; DF - Degree of freedom; MS - Mean Square

tween the lack of fit mean square and the estimation of experimental variance 24 and 24.53 for responses  $Y_1$  and  $Y_2$  are inferior to tabulated ( $^{0.05}F_{10,7}$ ); hence, the model is valid for both responses  $Y_1$  and  $Y_2$ .

### The response surfaces

The use of the NemrodW software<sup>15</sup> enabled us to obtain the response surfaces which in turn allow the determination of optimum conditions from 2D and 3D contours to guarantee maximum recovery % of phosphate concentration from both industrial and synthetic solutions.

It can be concluded from Figures 8–11 that the optimum conditions were quite efficient to trap 86.10 % recovered phosphates in industrial stream and 92.6 % in synthetic solution at pH of 10.89, time of reaction of 34.76 min, temperature of 25.23 °C and *R* of 2.25 with an insignificance effect for initial molar ratio *R* between Mg and PO<sub>4</sub> ions taking its value on the center point R= 2.25. The dependence of struvite precipitation and phosphate recovery was very clear through validated model to be highly influenced by time of reaction, temperature and pH of medium. For the fourth parameter, molar ratio between reactants was automatically adjusted to center point of studied range using applied software for model validation.

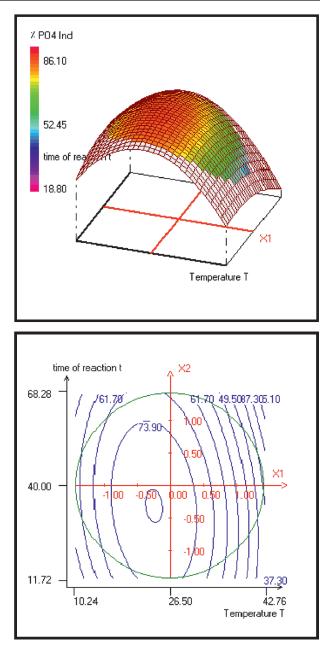


Fig. 8 – Predicted model: 3D and 2D contour plot showing the effect of temperature of precipitation and time of reaction on the response of %  $PO_4$   $Ind(Y_1)$ 

# Conclusions

A four factors Box-Behnken design was employed in order to model and optimize the chosen responses (%  $PO_4$  Ind, %  $PO_4$  Syn). According to the four factors fields, two valid models were established. It was clear that the maximum achieved percentage for phosphates recovered from synthetic solution as struvite was 92.6 %, which guarantees the optimized operating conditions to highly recover phosphates and forming struvite.

According to these models, the precipitation of phosphate salts and struvite at 25.23 °C and pH of

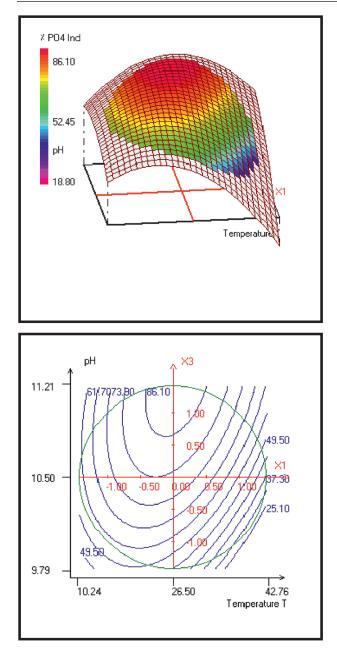


Fig. 9 – Predicted model: 3D and 2D contour plot showing the effect of temperature of precipitation and pH on the response of %  $PO_4$  Ind  $(Y_4)$ 

wastewater of 10.89 for a time of 34.76 minutes at initial molar ratio between Mg:  $PO_4$  of 2.25 giving %  $PO_4$  recovered of 86 % which was verified experimentally % recovered  $PO_4$  from industrial wastewater stream of 84.74 % for model verification. These results represent a good achievement of modeling and optimization of chemical precipitation

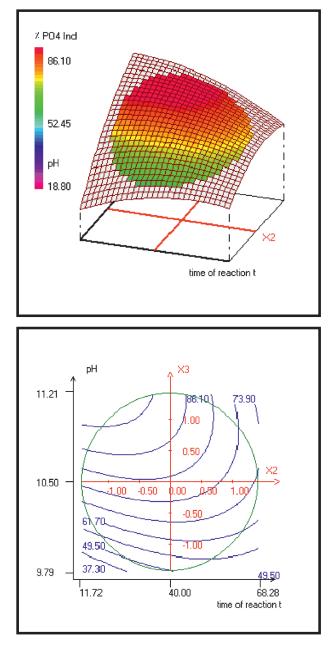


Fig. 10 – Predicted model: 3D and 2D contour plot showing the effect of time of reaction of precipitation and pH on the response of % PO, Ind  $(Y_y)$ 

and clarifying the influence of selected parameters and thus model validation with insignificance parameters. Finally, an easy, simple, and cost effective method for industrial wastewater treatment and precipitation of valuable fertilizer product rich in phosphorous, which is a depleting element in nature, would likely to be integrated.

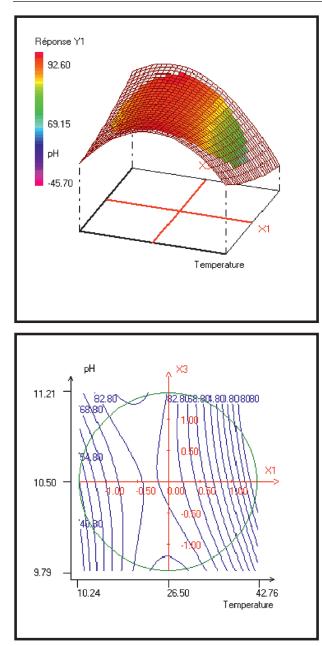


Fig. 11 – Predicted model: 3D and 2D contour plot showing the effect of temperature of precipitation and pH on the response of % PO<sub>4</sub> Syn (Y<sub>2</sub>)

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